

Raman Studies of Nanocrystalline CdS:O Film

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ABSTRACT

Oxygenated nanocrystalline CdS films show improved solar cell performance, but the physics and mechanism underlying this are not yet clearly understood. Raman study provides complementary information to the understanding obtained from other experimental investigations. A comprehensive analysis of the existing experimental data (including x-ray diffraction, transmission, transmission electron microscopy, and Raman) has led to the following conclusions: (1) The O-incorporation forms $\text{CdS}_{1-x}\text{O}_x$ alloy nano-particles. (2) The observed evolution of the electronic structure is the result of the interplay between the alloy and quantum confinement effect. (3) The blue-shift of the LO phonon Raman peak is primarily due to the alloying effect. (4) Some oxygen atoms have taken the interstitial sites.

1. Objectives

A poly-CdS film is commonly used as a window layer for the poly-CdTe thin film solar cell, which is one of the most efficient solar cell technologies practically available today. The use of a poly-CdS layer has some major drawbacks: such as, the diffusion of Te into CdS layer and the loss of light due to the above CdS band gap absorption. It has recently been demonstrated that oxygen-containing poly-CdS is able to effectively suppress these deficiencies and thus improve the cell performance[1]. Nevertheless, the underlying mechanism and physics are not yet clearly understood. On one hand, x-ray diffraction (XRD) measurements seem to indicate a polycrystalline to amorphous phase transition[1]. On the other hand, transmission electron microscopy (TEM) studies have revealed the formation of CdS related nano-particles with their sizes varying from a few hundred Å to a few tens Å, on increasing O content[2]. It is of great importance to know how the information of the structural studies relates to the electronic and optical properties.

For a semiconductor, the transition between the crystalline and amorphous phase often reflects in the relative intensity change of two Raman modes: a crystal mode (typically LO phonons) and an amorphous mode (a broad band)[3]. Another important effect associated with the structural transition is the red-shift and asymmetric broadening of the first order LO phonon Raman peak, which is usually explained as the grain size reduction causing a relaxation in the momentum selection rule (known as phonon confinement model)[4]. In oxygen implantated CdS thin films, the LO Raman peak has been found to blue-shift, on increasing oxygen dose, and the shift has been attributed to the bond-length reduction caused by oxygen atoms substituting sulphur atoms[5]. The blue-shift of the Raman

peak observed in our O-doped CdS films[1] is qualitatively similar to that reported for the O-implanted samples. A recent study on similar O-doped CdS films has suggested that the Raman linewidth dependence on O-doping level could be explained by the phonon confinement model.[6] In this work, we attempt to achieve a more comprehensive understanding of the electronic and optical properties of the O-doped CdS thin films by correlating the results of Raman study to other measurements (XRD, transmission, and TEM).

2. Technical Approach

Five O-doped CdS thin film samples, S1–S5, deposited at O_2/Ar ratios of 0, 1%, 2%, 3%, and 5%, were used in this work. The corresponding O compositions are 4.35%, 8.66%, 11.08%, 13.88%, and 22.73%, respectively. An undoped CdS single-crystal sample, S0, is used as a reference.

Raman spectra were measured at room temperature using ~ 70 mW 4579 Å line of an Ar^+ laser. The detection system included a SPEX 1403 double-grating spectrometer, a cooled RCA C31034 GaAs PMT and a Princeton Instruments Spect-10: 100R CCD.

3. Results and Accomplishments

As reported in Ref.[1], the XRD measurement has shown that the (0002) peak of the wurtzite CdS quickly diminishes on increasing O content, which, at first sight, would suggest that the material has become amorphous. Quantitatively, the peak position shifts slightly to the low angle side by 0.008° for S1 and 0.045° for S2, which roughly corresponds to lattice constant changes of $+3 \times 10^{-4}$ and $+2 \times 10^{-3}$. The increase in lattice constant, although rather small, indicates that the distribution of O atoms in the sample is not simple substitutional on the S sites. Otherwise, we would have observed a decrease in the lattice constant. The small lattice expansion seems to suggest the possibility that at least some O atoms take the interstitial sites instead.

Optical transmission measurements have also been performed on these samples.[1,2] The absorption edge for S1 is found to be *red-shifted* ($E_g = -0.06$ eV). Then, the absorption edge continuously *blue-shifts* (E_g up to +0.69 eV for S5) when more O is introduced. Such a behavior hints that the evolution cannot be simply a transform from polycrystalline to amorphous. The red-shift for S1 is qualitatively in agreement with the lattice dilatation observed above, but the magnitude of the shift far exceeded that estimated by considering the effect of a hydrostatic strain alone. Therefore, the lattice dilatation due to the interstitial occupation of O alone cannot be the primary cause for the absorption edge shift. Instead, the electronic structure change induced by O incorporation, likely through

the formation of $\text{CdS}_{1-x}\text{O}_x$ alloys, is expected to be more prominent, since CdO has a much lower band gap than that of CdS.

TEM study has offered another hint for the origin of the blue-shift in the absorption edge[2]. The microscopic structure of the low O sample (S1) is found to be consistent with the understanding that the CdS film is polycrystalline: it has an average domain size of 25 nm. However, the domain sizes in S3 are found to be substantially smaller, around 3-5 nm, which suggests that the observed blue-shift could be due to the quantum confinement effect of the nano-particle rather than amorphousization.

Raman study has provided complementary information to the understanding obtained from previously mentioned investigations. Figure 1 shows the first-order Raman spectra for S0–S4. The signal is too weak to be detected for S5 in this spectral region[1]. Three major apparent observations from Fig. 1 are (1) the peak intensity decreases on increasing O, (2) the linewidth increases significantly with respect to S0, and (3) the asymmetric broadening to the lower frequency side is rather small.

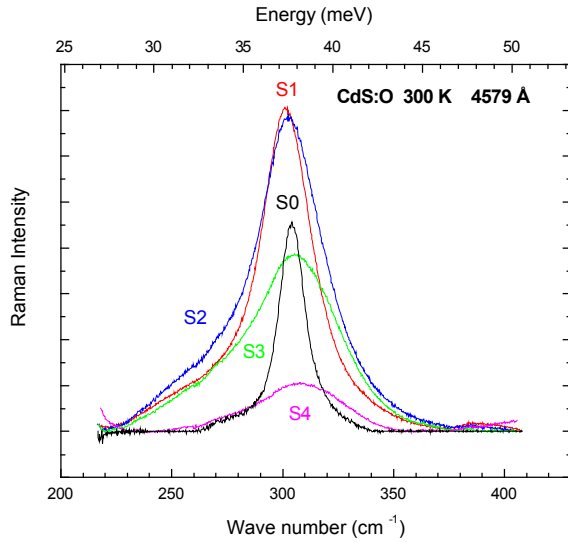


Fig. 1. Raman spectra of CdS:O thin films.

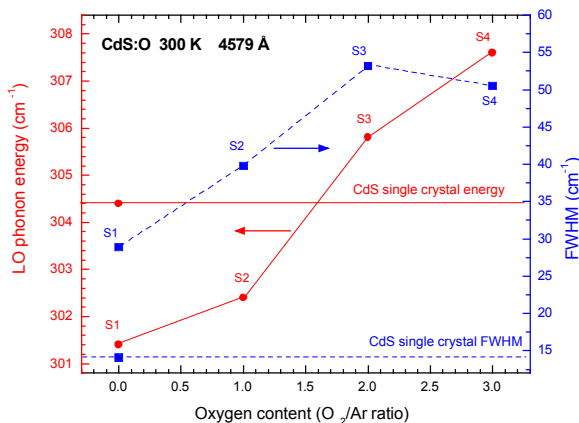


Fig. 2. Raman frequency and linewidth.

Figure 2 summarizes the peak positions and linewidths (measured by the full width at half maximums, FWHM) for S0–S4. Note that these spectra were measured by the CCD without moving the spectrometer between samples, to ensure the accuracy in the relative shift of the peak position. One intriguing finding is that the LO frequencies of the two lowest O samples are below that of bulk CdS, but the frequency monotonically increases with increasing O. The linewidth also increases with O, which is expected due to the enhanced structural fluctuation. The nearly symmetric lineshape and the direction of the peak shift make it inappropriate to explain the results using the frequently adopted phonon confinement model, as in Ref.[6]. Rather, we suggest that the initial red-shift could be related to the lattice dilatation due to interstitial O atoms, the tensile strain caused by the bond stretching near the grain boundary[7], and the strain generated by the substrate. The most important effect, the blue-shift, could be explained by the gradually increased incorporation of O atoms into the S sites, which results in more Cd-O bonds with a higher LO phonon frequency. This interpretation implies that the nano-particles in O-doped films are in fact $\text{CdS}_{1-x}\text{O}_x$ alloys.

4. Conclusions

A comprehensive examination of the results of different experimental investigations has led to the following conclusions: (1) The incorporation of oxygen into the polycrystalline CdS thin film does not simply transform the film into amorphous. Instead, it forms $\text{CdS}_{1-x}\text{O}_x$ alloy nano-particles. (2) The observed evolution of the electronic structure is the result of the interplay between the alloy and quantum confinement effect, with varying O doping level. (3) The blue-shift of the LO phonon Raman peak is primarily due to the alloying effect, but the mechanism for the initial red-shift remains unclear. (4) Some oxygen atoms have taken the interstitial sites, which might have some non-trivial effects on both electronic and vibrational properties of the film.

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